Introduction

• Impact of Wes Eckenfelder
  ▫ Personal
  ▫ Professional
Approach

• Control of Processes
  ▫ Equilibrium
  ▫ Kinetics
  ▫ Mixed

• Mechanistic Models
  ▫ Material balances
  ▫ Process descriptions
Overview

- Critical Processes (contaminant properties)
- Simple Model (contaminant properties + plant characteristics)
- Contaminant Fate (model, experience)
- Summary
Critical Processes

• Volatilization
  ▫ Equilibrium
    • Henry’s Law: $C_{\text{air}} = H C$
    • Vapor pressure/solubility
    • H affected by
      • temperature
      • other constituents
      • pH ($pK_a$)
Critical Processes

- **Volatilization**
  - **Kinetics**
    - \( r_{\text{vol}} = K_{\text{la}} \frac{(C - C_{\text{air}})}{H} \)
    - \( K_{\text{la}} \) affected by
      - temperature
      - other constituents (\( \alpha \))
Critical Processes

• **Volatilization**
  - **Mixed control model**
    - \( C_{air} = \frac{C_{0\ air}}{1 + (Q_{air} H / Q) (1 - \exp(- \varphi))} \) \( (\text{M&}E, \text{Tchobanoglous}) \)
    - “saturation factor”
      - \( \varphi = \frac{VK_{la}}{(Q_g H)} \)
      - \( \varphi = (\text{constants}) \text{OTE}/\text{H} \)
    - mass flow = \( Q_{air} C_{air} = (\text{if equilibrium}) Q_{air} HC \)
Critical Processes

• Sorption
  ▫ Terminology
    • adsorption
    • absorption
    • sorption
Critical Processes

- Sorption
  - Equilibrium
    - \( q = K_d C \)
    - \( K_d \) (500 L/kg, 50% sorbed at 2000 mg/L SS) (Verlicchi, Ternes)
    - Temperature/\( K_a \)
    - Correlations
      - \( K_{ow} \) (\( \log K_{ow} < 2.5, 2.5-4, >4.0 \)) (Jones, Birket)
      - solubility
      - molecular weight
      - polarity
Critical Processes

- Sorption
  - Kinetics
    - \( r_{sorb} = k_s X(C - q/K_d) \)
  - Control
    - Equilibrium in AS (Ternes)
      - high X
      - long enough HRT
    - Equilibrium in primary – long previous contact
Critical Processes

- Biodegradation
  - Terminology
    - biodegradation
    - mineralization
    - co-metabolism
  - Equilibrium
    - limited applicability
    - chemical redox equilibrium
Critical Processes

- Biodegradation

  - Kinetics
    - \( r_{bio} = k_{bio} \times C \)
    - Monod \( r_{bio} = \mu_{max} \times C / (K + C) \)
    - Rules of thumb (Joss)
      - < 0.1 L/g-d: hardly biodegradable
      - 0.1 – 1.0 L/g-d: moderately biodegradable
      - > 1.0 L/g-d: highly biodegradable
Critical Processes

- Biodegradation
  - Kinetics
    - $k_{bio}$
      - temperature
      - history of biomass
      - chain length
      - chain branching
      - substitution (halogens, sulfonate, methoxy, nitro)
    - size/solubility/$K_{ow}$
  - Control - Kinetics
Critical Processes

• Data sources
  • Pomies et al. (micropollutants)
  • Omil et al. (micropollutants)
  • Birkett and Lester (endocrine disrupting compounds)
  • Verlicchi et al. (pharmaceuticals)
  • Petrovic and Barceló (surfactants)
  • Choubert et al. (removals)
  • Martin Ruel, et al. (removals)
Simple Model

• Assumptions
  ▫ Completely mixed basin
  ▫ Diffused aeration
  ▫ Control
    • volatilization – equilibrium
    • sorption – equilibrium
    • biodegradation – kinetic
  ▫ Steady state
  ▫ Trace contaminant
Simple Model

• Derivation
  ▫ **Material balance:** \( \text{Acc} = \text{In} - \text{Out} + \text{Form} - \text{Lost} \)
  ▫ **Processes at SS:** \( o = QC^o - (QC + Q_{\text{air}}C_{\text{air}} + m_xq) + o - V r_{\text{bio}} \)
  ▫ **Process Eqns:** \( o = QC^o - (QC + Q_{\text{air}}HC + m_xK_dC ) + o - V k_{\text{bio}}XC \)
  ▫ **Rearrange:** \( C = C^o/(1 + Q_{\text{air}}H/Q + m_xK_d/Q + k_{\text{bio}}X HRT) \)
  ▫ **Biokinetics:** \( C = C^o/[1+Q_{\text{air}}H/Q+Y_{\text{obs}}(S^o-S)(K_d+k_{\text{bio}} SRT)] \)
Simple Model

• **Factors** \( C = C^0/[1 + Q_{air} \frac{H}{Q} + Y_{obs}(S^0 - S)(K_d + k_{bio} SRT)] \)
  - **Volutilization:** \( Q_{air} \frac{H}{Q} \)
    - if \( Q_{air} \frac{H}{Q} = 1 \), \( (Q_{air}/Q = 22.5) \)
      - \( H = 0.044 \)
      - \( H' = 1.1 \text{ L-atm/mole} \)
    - **Compare** (ME Tchobanoglous)

<table>
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<tr>
<th>Compound</th>
<th>H'</th>
<th>H</th>
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<tr>
<td>Chloroethene</td>
<td>64</td>
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<tr>
<td>Tetrachloromethane</td>
<td>28.6</td>
<td>1.17</td>
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<td>28.5</td>
<td>1.16</td>
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<td>t-1,2-Dichloroethene</td>
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<td>1,1,2,2-Tetrachloroethane</td>
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<td>0.02</td>
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Simple Model

• **Factors** \( C = C^0 / [1 + Q_{air} H / Q + Y_{obs} (S^0 - S)(K_d + k_{bio} SRT)] \)
  
  ▫ **Sorption:** \( Y_{obs} (S^0 - S)K_d \)
  
  ▪ if \( Y_{obs} (S^0 - S)K_d = 1 \)
    
    ▪ \( K_d = 17,500 \text{ L/kg} \)  
      \( (Y_{obs} = 0.3, (S^0 - S) = 190 \text{ mg/L}) \)
  
  ▪ **Compare** (Pomies)
    
    ▫ Estradiol, 170-2000
    ▫ Anthracene, 1493
    ▫ Pentachlorophenol, 2800
    ▫ Nonylphenol, 15,000
    ▫ Cd, 39,800
Simple Model

- **Factors** \( C = C_0 / [1 + Q_{\text{air}} H/Q + Y_{\text{obs}} (S_0 - S)(K_d + k_{\text{bio}} SRT)] \)
  - **Biodegradation**: \( Y_{\text{obs}} (S_0 - S) k_{\text{bio}} SRT \)
    - if \( Y_{\text{obs}} (S_0 - S) k_{\text{bio}} SRT = 1 \)
      - \( k_{\text{bio}} = 1.75 \) L/g-d \( (Y_{\text{obs}} = 0.3, (S_0 - S) = 190 \) mg/L, SRT = 10 d)
    - **Compare** (Pomies, with \( X = 2 \) g/L)
      - Estradiol, 6-350
      - Ibuprofen, 1.3-38
      - Octylphenol, 1.1 - 32
Contaminant Fate

• Primary Sedimentation
  ▫ Sorption primary process
  ▫ Equilibrium control likely
  ▫ Removal = $SS^0 \cdot R_{ss} \cdot K_d / (1 + SS^0 \cdot K_d)$
  ▫ Observations
    • 25% removal of typical surfactants (Petrovic)
    • Little removal reported
      • $K_d < 500$ L/kg (Ternes)
        (5% removal for $SS^0 = 200$ mg/L, $R_{ss} = 0.60$)
      • $\log K_{ow} < 4.0$ (Birkett) ($K_d \approx 1000 – 3000$ L/Kg)
        (10-22% removal)
Contaminant Fate

- **Activated Sludge**
  - **SRT**
    - Promotes biodegradation
    - \( Y_{\text{obs}} (S^o - S) k_{\text{bioSRT}} \)
    - Population changes
      - Nitrifiers (co-metabolism)
      - Slow growing heterotrophs
Contaminant Fate

• Activated Sludge
  ▫ SRT
    • Promotes volatilization ($Q_{\text{air}}H/Q$)
      • more oxygen required, $Q_{\text{air}}$ increases,
        ▫ less synthesis more oxidation
        ▫ nitrification oxygen demand
        ▫ mitigated by higher $\alpha$
Contaminant Fate

- **Activated Sludge**
  - **SRT**
    - Hinders sorption \( Y_{\text{obs}}(S^o - S)K_d \)
    - less solids synthesized
    - Possible change in solids ability to sorb

\[ \text{Substrate} \rightarrow \text{Energy} \]
\[ \text{Energy} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]
\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Nutrients} \rightarrow \text{Biomass} \]

\[ \text{O}_2 \rightarrow \text{Substrate} \]
Contaminant Fate

- Activated Sludge
  - SRT
  - Observations
    - Generally removals increase
      
(Zeng, Pomies, Leu)
Contaminant Fate

- Activated Sludge
  - SRT
  - Observations
    - Some correlations with nitrification (Verlicchi, Zhou, Vieno)
      - co-metabolism (Roh, Sipma)
      - nitrification inhibitors reduce removal (Batt, Roh)
      - removals related to extent of nitrification (Vieno)
Contaminant Fate

• Activated Sludge
  ▫ Aeration Intensity
    • Diffused (for equilibrium: $Q_{air}H/Q$)
      • bubble size
      • depth
      • SRT ($m_{o2}$)
  ▫ Surface ($K_{la}$ HRT)
    • may promote low H release vs. diffused
      ▸ kinetic control
      ▸ remove equilibrium limit on low H
        $\varphi = VK_{la}/(Q_gH)$
    • SRT ($m_{o2}$)
Contaminant Fate

- **Activated Sludge**
  - Mixing (plug flow to completely mixed)
    - high C, higher volatilization ($Q_{air \cdot HC}$)
  - Enhanced P removal (low SRT)
    - Promotes sorption ($Y_{obs}(S^o - S)$)
    - Reduces biodegradation ($Y_{obs}(S^o - S)SRT$)
    - Reduces volatilization ($Q_{air \cdot HC}$)
  - Temperature
    - Promote biodegradation, volatilization
    - Hinder sorption
Contaminant Fate

- **Activated Sludge**
  - Membrane biological reactors (Siegrist)
    - Lower effluent SS, promote sorption for high $K_d$
    - Higher SRT (+bio., + vol., - sorption)
    - $Q_{air}/Q$ higher, promote volatilization
  - Population distribution different
- **Other biological treatment** – similar (Choubert)
Contaminant Fate

- Disinfection
  - Chlorination
    - Free chlorine
    - potential oxidation
    - potential byproduct formation
  - Combined chlorine
    - general reduced reactivity
    - potential to form NDMA
Contaminant Fate

• Disinfection
  ▫ Ultraviolet
    • Potential photolysis
    • Potential reaction with products of photolysis
Summary

- Fate determined by
  - Contaminant Properties ($H$, $K_d$, $k_{bio}$)
  - Plant Characteristics ($SRT$, $Q_{air}$, aeration type)
Summary

- Indirect effects possible
  - SRT/$m_{o2}/Q_{air}/$volatilization
  - SRT/$m_{ss}/$sorption
  - SRT/nitrification/biodegradation
  - Basin depth/$Q_{air}/$volatilization
  - pH change/$H, K_d/volatilization, sorption$
Summary

• Mechanistic models are useful
References


References


